

A REVIEW OF NANOPOROUS MATERIALS DERIVED FROM COVALENT ORGANIC FRAMEWORKS

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ABSTRACT

The implementation of nanoporous materials is becoming increasingly more prevalent due to their unique characteristics, which make them highly applicable in a multitude of different functionalities. Covalent Organic Frameworks (COFs) are one of the new types of nanoporous material constructed from covalently bonded non-metals. COFs exhibit several advantages over conventional nanoporous materials such as low density, high thermal stability and the framework can be tailored for specific applications. This paper reviews recent works on synthesis, characterisation and applications of this new class of nanoporous materials. It is obvious from various studies that 3-dimensional COFs can, at least, compete with established nanoporous materials such as zeolite and metal organic frameworks (MOFs) in terms of potential for H₂ storage, if not improve upon them. While previous studies focused on applying COFs for hydrogen storage, it is postulated that COFs can be further developed for various chemical engineering applications such as gas storage, separation processes, and catalytic reactions.

Keywords: Adsorption; Covalent Organic Frameworks; Gas Storage; Nanoporous Materials

1.0 INTRODUCTION

One of the ultimate goals of chemists, material scientists and chemical engineers in terms of sustainable technologies is to develop an efficient hydrogen storage material in order to initiate the global hydrogen economy. A commonly used standard to develop such a material is the United States Department of Energy target of a nanoporous material capable of storing up to 6 wt% of hydrogen at ambient temperature and pressure. This challenge drives scientists and engineers to synthesize novel lightweight nanoporous materials to replace conventional porous materials such as activated carbon, zeolite and silicate frameworks for such application.

Yaghi *et al.* [1] in 1995 first published work regarding modular metal organic frameworks (MOFs) and provided the stepping stone towards the development of organic frameworks for various applications, including hydrogen storage. MOFs are composed of metal or metal oxide vertices connected by organic linker molecules containing functional groups, which coordinate with the metal corners and thus complete the MOF unit. These materials can be composed of numerous metal, metal oxide and organic linker molecule combinations, thus enabling the formulation of many application specific MOFs. Precise coordination geometries between the organic linker molecules and metal vertices result in highly-ordered, periodic porous structures [2]. Such porous materials are characterised by pore

dimension, low density, high thermal stability, high surface area and crystalline [3;4]. MOFs are well-established nanoporous materials and used in adsorption, separation, catalysis, extraction and gas storage technologies. However, they still have a significant drawback in terms of presence of 'heavy' metal atoms within their frameworks which add weight in the structure without enhancing hydrogen storage capacity.

An obvious improvement in the gravimetric capacity of these nanoporous materials can occur by substituting the metal cluster with another lighter building block or by a novel family of materials that will exhibit the large surface area and the aromaticity of the organic linkers that MOFs have, but without the drawback of the presence of heavy metals [5]. In this sense, covalent organic frameworks (COFs) provide an alternative to improve on this characteristic since their molecular frameworks are made up of light elements (carbon, boron, hydrogen and oxygen) that reduce the relative weight of the structure. The term "covalent organic framework" refers to an extended covalent organic network having clusters connected by linking groups [6]. COFs were discovered by Côté and co-workers in 2005 whilst searching for a new porous, crystalline material composed of building blocks linked together by strong bonds. Networks which are assembled via strong covalent bonds exhibit enhanced stability over many coordinatively linked materials [7].

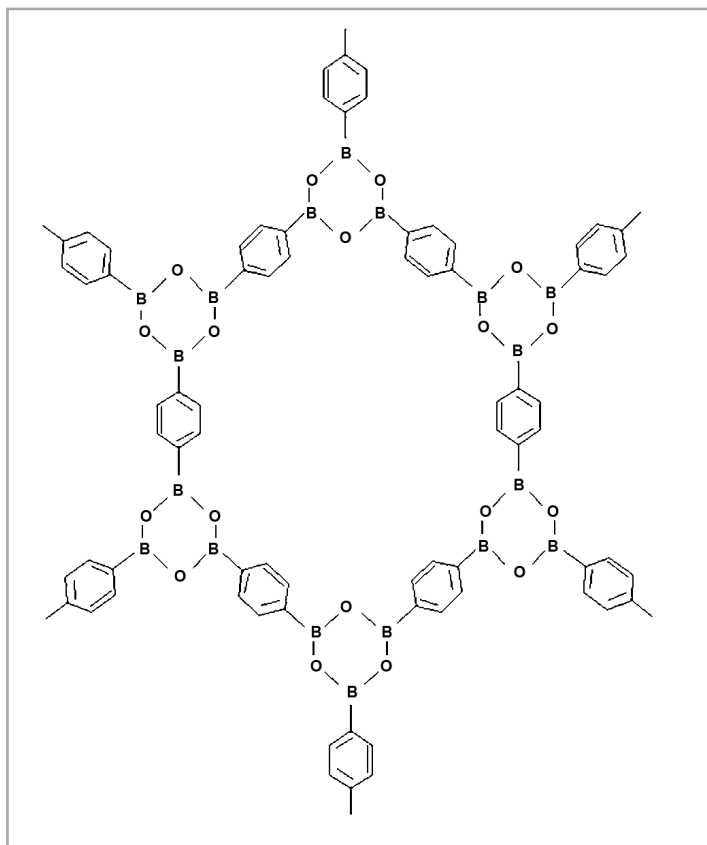


Figure 1: COF-1 structure [8]

The first synthesized COF, named COF-1 ($(C_3H_2BO)_6$ and $(C_9H_{12})_6$) (Figure 1), is obtained from the molecular dehydration of 1,4-benzenediboronic acid (BDDBA) [8]. The reversible formation of COFs, specifically COF-1, allows for the reordering of the framework yielding a material of significantly greater structural organisation than that found in rigid polymers. Such formation enables specific manipulation and tailoring of the framework hence enabling the development of reaction/process specific COFs. The porous frameworks have high thermal and chemical stability with surface areas, which surpass those of the well-established porous zeolite and silicate frameworks.

The development of COFs, while still in its early stages, has exhibited great potential for application in the field of hydrogen storage. The aim of this review is to critically assess and summarise the recent works concerning synthesis, characterisation and application of COFs for hydrogen storage, as well as to hypothesise on other areas for future development and application within the realm of chemical engineering processes.

2.0 SYNTHESIS OF COFs

Intriguingly, COFs can exist as one, two and three dimensional structures. Two dimensional structures resemble layered graphite composed of graphene sheets [9], whereas three dimensional COFs are composed of triangular and tetrahedral nodes; COF-102, 103, 105 and 108 [10]. COF-102 and 103 have similar characteristics except that COF-103 uses silicon atoms at the tetrahedral nodes rather than carbon. COF-NT, a one dimensional COF, also known as the armchair or zig-zag, is constructed by

rolling a COF layer in a particular direction in a manner similar to that of carbon nanotubes [9]. It is widely known that Omar M. Yaghi's group are the pioneers behind the synthesis of COFs via reticular chemistry (linking molecular building blocks into extended structures by strong covalent bonds [11]). Table 1 presents existing COFs synthesised by the Yaghi group to date. The synthesis temperatures to produce these COF systems are relatively low ($< 150^\circ\text{C}$) and this may present another plus point in terms of safety considerations.

Besides the Yaghi group, other researchers [12-15] have also synthesized COF variants. Kuhn *et al.* [12] synthesized a new class of high performance polymer frameworks with regular and irregular porosity formed from simple, cheap, and abundant aromatic nitriles via dynamic trimerisation in ionothermal conditions (molten zinc chloride at high temperature). This new class of frameworks is designated as covalent triazine-based framework (CTF-1) which resembles the boron oxide-based (COF-1) and has a surface area of up to $2475\text{ m}^2\text{ g}^{-1}$ and a total pore volume of $2.44\text{ cm}^3\text{ g}^{-1}$.

Tilford *et al.* [14] tailored the pore dimensions and COF environment through the condensation of dialkyl-substituted bis-diols with triboronic acids. In general terms, they incorporated hydrophobic and sterically bulky groups (alkyl groups, *e.g.* methyl, ethyl and propyl) in the pores while maintaining the same basic COF structure. They found that modification of the pore interior with increasingly larger alkyl groups caused a decline in nitrogen uptake, but an increase in the molar amount of hydrogen adsorbed by the network.

Another COF variant is the Surface Covalent Organic Framework (SCOF), which has been developed and synthesized by Zwaneveld *et al.* [15]. SCOFs are functionally and structural controllable due to their complimentary bicomponent composition; HHTP (2,3,6,7,10,11-hexahydroxytriphenylene) and BDDBA (benzenediboronic acid). The networks produced are connected by boronate covalent bonds generated by the molecular dehydration of BDDBA with three boronic acid molecules reacting to form a six-membered B_3O_3 rings, SCOF-1, and the condensation reaction of BDDBA and HHTP forming dioxaborate heterocycles, SCOF-2. It is of note that the quality of the network is highly dependent upon the removal of impurities and water during synthesis.

3.0 CHARACTERISTICS OF COFs

3.1 Density and Thermal Stability

One of the major obstacles to the extensive use of hydrogen as a fuel is the lack of lightweight storage materials with high thermal stability capable of storing large volumes of hydrogen gas. COFs have been reported to be able to withstand temperatures as high as 600°C [8]. Metal hydrides have been considered as practical means for high pressure liquid hydrogen storage using physisorption according to the works of Frost and Snurr [2], however this approach has inherent problems including hydrogen embrittlement and handling issues. COFs have greater pore size control and most importantly lower densities than MOFs, *e.g.* COF-108 has a density of 0.17 g cm^{-3} compared to MOF-5 and

MOF-177 with respective densities of 0.59 and 0.42 g cm⁻³. Another characteristic of COFs is their high thermal resistivity, which derives from their strong covalently bonded framework and makes their application in high-temperature processes viable.

3.2 Surface Area and Pore Characteristics

Surface area, or specific surface area, is one of the major factors that influences the characteristics, or behavior, of many materials and can be used as an indicator to determine the efficiency of the material with respect to hydrogen adsorption. Thus, it can be said that, a porous material with a large surface area and good adsorption characteristics govern the volume of adsorbate by maximising the adsorption capability [16]. COFs are porous materials with particularly large surface areas; the specific surface areas of COF-5, COF-102 and COF-103 are 1590, 3472 and 4210 m² g⁻¹ respectively, which are larger than zeolite Y (904 m² g⁻¹) [10;17] and double that of MCM-41 (Mobile Crystalline Material 41) [18]. The latest synthesized COFs; COF-202 was found to have a BET surface area and Dubinin-Radushkevich pore volume of 2690 m² g⁻¹ and 1.09 cm³ g⁻¹, respectively [11]. Table 2 compares the textural characteristics of existing COFs to conventional porous materials. The intended application of COF systems for gas capture or storage is clearly reflected by their small pore sizes which are predominantly microporous (< 2 nm or < 20 Angstrom) with the exception of COF-5, COF-10 and TP-COF.

Adsorbent specific area can be calculated from the adsorption data of nitrogen vapour at 77 K using a linear form of Brunauer-Emmett-Teller (BET) surface area equation for non-porous, macroporous and mesoporous COFs. Isothermal correlation of the Langmuir surface area equation for microporous materials is used to infer the pore characteristics, *e.g.* COF-5 contains mesopores (0.998 cm³ g⁻¹) and has a surface area of 1590 m² g⁻¹ [19]. In addition to surface area, pore volume is also considered as one of the main factors in achieving good adsorption with varying pressure. The level of solid-fluid interaction will dictate the quantity and efficiency in capturing gas molecules.

Pore distribution and size are vital components of a porous material, because the function and adsorption strength of the different sized pores changes with process conditions. Increasing adsorbate molecule size results in decreasing adsorption capacity due to the exclusion of access to the smaller pores [20]. Hence, the pore size must be tailored to suit the size of the adsorbate molecules. El-Kaderi *et al.* [10] reported the synthesis of COF-108: a crystalline mesoporous material with two different primary pore sizes of 15.2 Å and 29.6 Å, and a carbon Van der Waals radius of 1.7 Å. It is preferential for reaction-based porous materials to have either meso- or micropores, because the larger meso pores act to channel and transport the adsorbate molecules to the micropores, which are filled; once the micropores are full, then the mesopores are progressively filled.

Further to this, three dimensional simulation work by Garberoglio [17] on COF-102, -103, -105 and -108 show that the

Table 1: Recent works conducted by Yaghi group on synthesis of COFs

Researchers	Designation	Synthesis process	Synthesis condition
Côté <i>et al.</i> , 2005	COF-1	Dehydration of 1,4 benzenediboronic acid (BDBA)	120°C for 72 hours
Côté <i>et al.</i> , 2005	COF-5	Dehydration of phenylboronic acid and HHTP*	100°C for 72 hours
Côté <i>et al.</i> , 2007	COF-6	Co-condensation of HHTP * and 1,3,5-benzenetriboronic acid (BTBA)	85°C for 48 to 120 hours
Côté <i>et al.</i> , 2007	COF-8	Co-condensation of HHTP * and 1,3,5-benzenetris (4-phenylboronic acid) (BTPA)	85°C for 48 to 120 hours
Côté <i>et al.</i> , 2007	COF-10	Co-condensation of HHTP * and 4,4'-biphenyldiboronic acid (BPDA)	85°C for 72 hours
El-Kaderi <i>et al.</i> , 2007	COF-102 and COF-103	Self-condensation of tetra(4-dihydroxyborylphenyl) methane (TBPM) or silane analog (TBPS) and HHTP *	85°C for 96 hours
El-Kaderi <i>et al.</i> , 2007	COF-105 and COF-108	Co-condensation of TBPM or TBPS with HHTP *	85°C for 96 hours
Hunt <i>et al.</i> , 2008	COF-202	Condensation of tert-butyldisilane triol with monotopic boronic acid to form a high symmetry borosilicate cage.	120°C for 72 hours

* HHTP = 2, 3, 6, 7, 10, 11-hexahydroxytriphenylene

uptake of adsorbate molecules, namely hydrogen gas, at 77 K and low pressures is better for COF-102 and -103 due to better solid-fluid interactions. Hence, the more compact the microscopic structure the better the solid-fluid interactions and the greater the adsorption capability. At low pressures, large pore sizes in the macroscopic range (> 50 nm) are detrimental to the adsorption capability, because the solid-fluid interactions are insufficiently strong to ensure adherence of the adsorbate molecules to the porous surface. According to Garberoglio *et al.*²¹ and Latroche *et al.* [22] this is a common problem inherent in MOFs. However, at high pressure, the inverse trend is found with respect to COF-102, -103, -105 and -108 in which COFs with larger pore size have higher uptakes than the smaller ones (COF-102 and -103). This is due to the increased pressure driving the adsorbate molecules deeper into the macropores and sufficiently close to the surface

to facilitate sufficiently strong solid-fluid interactions to cause adsorption.

Although cryogenic results evidently indicate that COFs have superior uptakes, it is under ambient conditions that the uptake is of greater importance; due to the high costs associated with cryogenics and the consequent cost saving benefits of ambient condition storage. Unfortunately, to date, no high uptake porous materials exist [17]. A primary advantage that COFs have over MOFs and zeolites is that COFs have no latent edges (minutely-sized edges not visible to the naked eyes) within their three dimensional arrangement, thus optimising access to the faces and edges of the molecular framework units., which means larger surface areas and statistically increases the number of available adsorption sites at the aromatic ring centres [17].

Table 2: Comparison between textural characteristics of COF systems and conventional nanoporous systems

Designation	Surface area (m ² g ⁻¹)	Pore size (Å)	Reference(s)
COF-1	711	15.0	8
COF-5	1590	27.0	19,8
COF-6	980*	8.6	19,33
COF-8	1400*	16.4	19,33
COF-10	2080*	31.7	19,33
COF-18 Å	1260	18	4,7
COF-102	3472	8.9	10
COF-103	4210	9.6	10
COF-202	2690#	11.0	11
TP-COF	868	31.4	40
26 Å MCM-41	680	26.0	8
32 Å MCM-41	1140	32	18
Carbon Black Pearls, BP700	170	212.0	38
Carbon Black Pearls, BP2000	520	456.0	38
Zeolite Y	904	7.4	10,39
MOF-177	4500	11.8	4,37
MOF-5 @ IRMOF-1	2900	15.2	17,37
CTF-1	791	12.0	12
MIL-53 (Al)	1020	6.4	37
MIL-101	4100	-	10

*Langmuir surface area; generally higher than BET surface area

measured with argon

3.3 Enhancing Adsorption Capacity

The enhancement of adsorption capability at ambient conditions is a focal point of COFs research, because it is essentially the limiting step in its wider implementation. Methods such as increased pore density, increased adsorption energy, the use of atomic hydrogen, increased carbon bridging and spillover technology (interphase diffusion of adsorbed active species) induce greater gas uptake. However, all of these methods have their limitations and they are discussed in the following.

Increasing the pore density appears to be comparatively simple since the COF structures can be manipulated to generate a high density of smaller pores, which inherently causes an increase in surface area and hence provides greater storage capability. Even so, this requires systematic synthesis and a large degree of control over the reaction mechanism and the synthesis of specific reagents, all of which, ultimately, increase synthesis and processing costs. Adjusting the adsorption energy through enhanced activation of the COFs surface improves the solid-fluid interaction and increases the likelihood of adsorbate molecule capture. Bhatia and Myers [23] conducted work with integration of simulation components, suggested that increasing the value to 15 kJ mol^{-1} is necessary to improve adsorption. In another separate development, experimental findings reported by Dinca *et al.* [24;25] showed that adsorption isotherms measured at 77 and 87 K indicate high H_2 adsorption enthalpies in the range 7.0–9.5 kJ/mol, depending on the degree of loading.

In order to facilitate greater adsorption, it will require much greater interaction energy throughout the COFs structure to generate any significant improvement in the adsorbate uptake. Another means to increase the adsorption energy is through carbonisation of the carbon bridges [26]. Although high temperatures in excess of 250°C are required for this process, COFs are thermally stable to well above this temperature and this provides a viable method to activate the adsorption surface. Experimental work conducted by Li and Yang [26] has shown that the molecular hydrogen take-up of COF-1 increases by 2.6 times and the bridge structure remains unsaturated, thereby maintaining the original adsorption sites and structure. This approach can also be used to generate a greater degree of bridging thus enabling secondary spillover and providing an increased number of adsorption sites which combined with the use of atomic hydrogen provides an increase in overall hydrogen adsorption.

Another approach to overcome the problem of low uptake and the difficulties associated with increasing adsorption energy is to increase the number of available adsorption sites and using all existing sites to their full potential. [16] Morris and Wheatley [16] suggest the use of atomic rather than molecular hydrogen, which would improve the use of the available pore space since the smaller atoms can penetrate deeper into the pores. Choi *et al.* [27] studied hydrogen storage mechanisms on pure and metal ion-decorated COFs via first principles calculations and discovered that the H_2 binding characteristics of pure COFs are very similar to those of MOFs. The research suggest that using Li^+ and Mg^{2+} ions yield more advantageous activated structures, but at the price of higher COFs weights which can be construed as a significant drawback. In a theoretical study, Kim *et al.* [28] inserted pillar molecules (pyridine) between the organic layers of COF-1 to improve the physisorption ability for hydrogen molecules in which they

observed puckering in the cluster model of the COF, which were caused by binding of pyridine molecules.

4.0 APPLICATIONS OF COFs

4.1 Hydrogen Storage

One intended application of COFs is for H_2 storage. Judging by recent research, it can be generally agreed that 3-D COFs are most advantageous compared to conventional storage materials. Han *et al.* [29] used grand canonical Monte Carlo (GCMC) simulations to hypothesise that the best COFs for hydrogen storage are COF-105 and COF-108, each of which lead to maximum excess H_2 uptakes of 10 wt % at 77 K (the highest value reported for associative H_2 storage of any material). The very low uptake temperature at 77 K is the stumbling block for commercialisation of COFs. In light of this, it has been suggested that in order to obtain high H_2 uptake at 300 K, doping of COFs with electropositive elements such as Li, Na, K should be carried out in order to increase H_2 binding energy. [30]

In a theoretical study, Klontzas *et al.* [31] reported that the gravimetric uptake for COF-108 reached the value of 21 wt % at 77 K and 100 bar conditions and the very promising value of 4.5 wt % in room temperature and 100 bar conditions. They also indicated the gravimetric uptake of COFs is in some cases 2 times larger than that of the best known MOFs while the volumetric results remain comparable. Kuhn *et al.* [12] experimentally found that covalent triazine-based framework could adsorb up to 1.55wt% H_2 at 1.00 bar and 77 K while Tilford *et al.* [14] reported that their customised COFs could store up to 1.5 wt% H_2 at 77K and 760mm Hg. A general consensus from all these combined theoretical and experimental studies shows that 3-D COFs can, at least, compete with established MOFs in terms of potential for H_2 storage, if not improve upon them. Two-dimensional COFs, however, are relatively ineffective and less likely to be used for H_2 storage in the future according to Garberoglio and Vallauri [32], who conducted computer simulation and found that the quantity of H_2 adsorbed in these materials was generally half that adsorbed by other organic frameworks under the same conditions, either on both gravimetric and volumetric bases.

4.2 Carbon Dioxide and Methane Storage

Recent studies have indicated that COFs have high potential for the storing of other gases such as CO_2 and CH_4 . Barbarao and Jiang [33] reported that COF-102 exhibited CO_2 high capacity at considerably low pressures. They further reported that COF-102 could reach CO_2 saturation ($> 13 \text{ mmol/cm}^3$) at a pressure of approximately 1000 kPa, which is less than half of the saturation pressures observed for MOFs for similar volumetric saturation. This indicates that COFs can be further developed to be incorporated into more effective and safer CO_2 sequestration systems.

Methane is a major component of natural gas and is a very promising fuel source. However, it is found normally in the gas phase, which makes it difficult to store. Currently, methane is stored in pressurised containers to maintain it in its liquid phase at ambient temperatures. This phase change and added safety comes at a high price; the installation of multiple safety procedures to guard against the possibility of leakage and consequent possible explosion is vital. COFs offer an alternative means to storage of

methane gas. The COFs enable storage of the gas in large quantities due to their extensive porous structures. Garberoglio [17] reported that COF-102 had the potential to meet or even exceed the DOE target of 180 cm³ (STP)/cm³ at 35 bar for methane adsorption. It was also found that methane adsorption in various COFs revealed the presence of a large volume with strong interaction energy in COF-102. Both studies by Barbarao and Jiang [33] as well as Garberoglio [17] observed that the packing of atoms in COF-102 was rather compact and, hence, has a significant overlap of spaces with attractive interaction with carbon dioxide molecules.

COFs have also been considered for the storage of other hydrocarbons, but it is possible that COFs could be used for general gas storage, including medical purposes (*e.g.* nitric oxide and oxygen), and as a way to store environmentally hazardous gases (*e.g.* carbon monoxide, ammonia, and sulphur dioxide) on a long term basis to help preserve our world and health.[16] Essentially the application of COFs on a large industrial scale is not unimaginable, but it will require further research and tailoring of existing COF technology.

4.3 Catalytic Support/Carrier

The ideal catalyst carrier is a porous, inert substrate with a large surface area, added benefits include chemical and heat resistance. Based on this criterion, COF would make an ideal catalyst carrier and its ability to be tailored would ensure that optimised catalyst loading is possible, irrespective of the catalyst size or shape, ensuring catalysis is performed effectively. The lightweight character of COFs would also enable a wider application as a catalyst carrier. Lino *et al.* [34] reported that 2-dimensional COF extended sheet systems could be rolled up to form stable nanotubes which could be applied as molecular filters/carriers, gas storage and building blocks for 3-dimensional structures.

4.4 Separation Processes and Other Applications

Separation is the process of dividing a mixture into two or more components, which is significant in the industrial sector. On an industrial level, separation constitutes enrichment, concentration, purification, refining and isolation [35] and may involve adsorption, decantation, filtration and drying. Ideally, one would wish to have a cheap, simple, easy to maintain and highly effective separation process, but in reality one finds that a compromise must be reached. COFs offer a tailorable, highly resistant, lightweight porous substrate, which can be activated to optimise separation of multi-component mixtures, which would make them an ideal candidate for use in the oil and gas industry.

Other modern technologies, including membranes and saline separation processes as well as bioreaction could benefit from the development of tailored COFs. Membrane and saline technologies require pore sizes to be of specific sizes so as to prevent ions passing through them; COFs could be tailored to selectively prevent ionic passage. COFs could be used in bioreactors, which require the immobilisation of microorganisms and enzymes on the surface of porous inert substrates. Coupled with the need for large surface areas is the requirement of a bimodal pore size distribution, whereby the smaller and larger pores act as immobilisation sites and transport channels for the carrier fluid, respectively [36]. However, it should be noted that saline separation and bioreaction processes involve presence of water, which can reverse the synthesis of COF frameworks and subsequently breaks them into starting materials. As such, extensive experimental studies to determine the state of COF frameworks in liquid flows should be conducted to shed light on this issue.

5.0 CONCLUSION

COFs, while mainly used for hydrogen storage, have great potential in other fields including catalysis and separation due to their highly desirable textural characteristics and varied framework structures. The physicochemical properties of COFs mean that their application is viable in many modern industrial processes, although it has yet to be proven that COFs are comprehensively superior to zeolites and MOFs in the long term. Preliminary technical studies have shown the huge potential of COFs in storing H₂, CO₂ and CH₄, which indicate their importance within the field of energy and environmental sustainable technologies. While there have been a multitude of studies on the effectiveness of COFs, studies on other aspects such as economics as well as environmental implications of using them in existing process systems are lacking. This is crucial since 3-D COFs are relatively more complicated and more expensive to produce. Further strides need to be taken to develop this highly promising group of compounds and enable process specific tailoring to be achieved without compromising cost-effectiveness and environmental sustainability, which many previously considered gas storage materials have failed in the past.

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